EXHIBIT A

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Smoothing

In many experiments in physical science, the true signal amplitudes (y-axis values) change rather smoothly as a function of the x-axis values, whereas many kinds of noise are seen as rapid, random changes in amplitude from point to point within the signal. In the latter situation it is common practice to attempt to reduce the noise by a process called *smoothing*. In smoothing, the data points of a signal are modified so that individual points that are higher than the immediately adjacent points (presumably because of noise) are reduced, and points that are lower than the adjacent points are increased. This naturally leads to a smoother signal. As long as the true underlying signal is actually smooth, then the true signal will not be much distorted by smoothing, but the noise will be reduced.

The simplest smoothing algorithm is the *rectangular* or *unweighted sliding-average smooth*; it simply replaces each point in the signal with the average of *m* adjacent points, where *m* is a positive integer called the *smooth width*. For example, for a 3-point smooth (*m*=3):

$$S_j = \frac{Y_{j-1} + Y_j + Y_{j+1}}{3}$$

for j=2 to n-1, where S_j the j^{th} point in the smoothed signal, Y_j the j^{th} point in the original signal, and n is the total number of points in the signal. Similar smooth operations can be constructed for any desired smooth width, *m*. Usually *m* is an odd number. The reduction in random noise is approximately the square root of *m*.

The *triangular smooth* is like the rectangular smooth, above, except that it implements a weighted smoothing function. For a 5-point smooth (*m*=5):

$$S_j = \frac{Y_{j-2} + 2Y_{j-1} + 3Y_j + 2Y_{j+1} + Y_{j+2}}{9}$$

for j=3 to n-2, and similarly for other smooth widths. This is equivalent to two passes of an 3-point rectangular smooth. For peak-type signals, the triangular smooth is better than the rectangular, in that it produces less peak distortion (attenuation and broadening) for a given degree of noise reduction.

Smoothing operations can be applied more than once: that is, a previously-smoothed signal can be smoothed again. In some cases this can be useful; however, the noise reduction is much less in each successive smooth.

An example of smoothing is shown in Figure 4. The left half of this signal is a noisy peak. The right half is the same peak after undergoing a triangular smoothing algorithm. The noise is greatly reduced while the peak itself is hardly changed. Smoothing increases the signal-to-noise ratio and allows the signal characteristics (peak position, height, width, area, etc.) to be measured more accurately, especially when computer-automated methods of locating and measuring peaks are being employed.

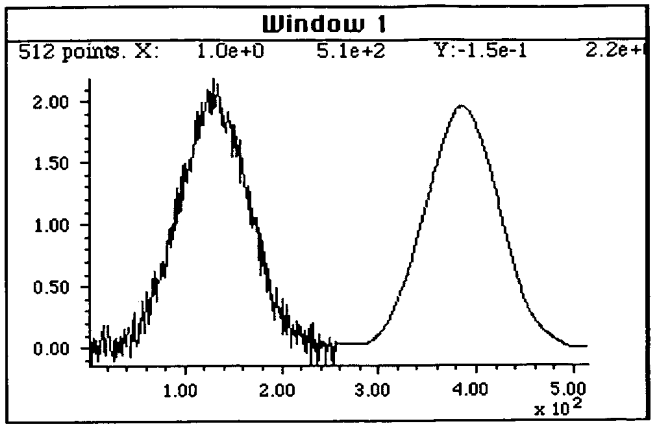
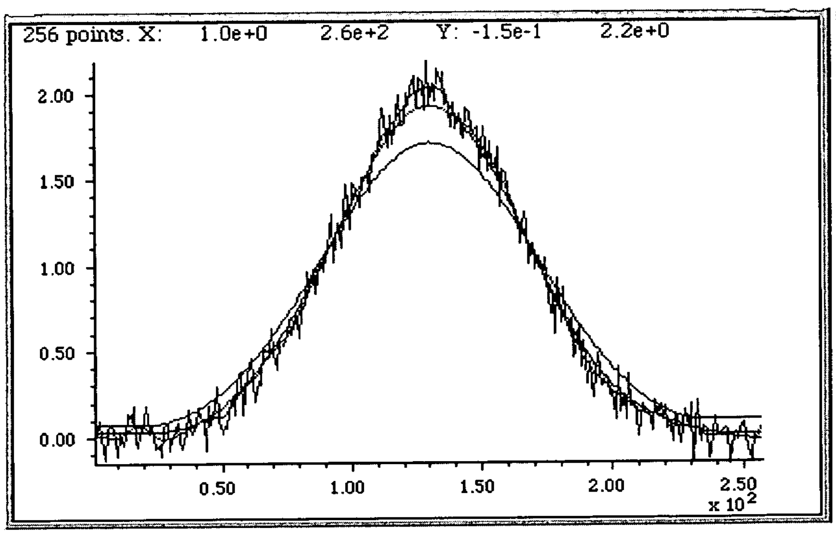


Figure 4. The left half of this signal is a noisy peak. The right half is the same peak after undergoing a ***smoothing*** *algorithm. The noise is greatly reduced while the peak itself is hardly changed, making it easier to measure the peak position, height, and width.*

The larger the smooth width, the greater the noise reduction, but also the greater the possibility that the signal will be distorted by the smoothing operation. The optimum choice of smooth width depends upon the width and shape of the signal and the digitization interval. For peak-type signals, the critical factor is the *smoothing ratio*, the ratio between the smooth width m and the number of points in the half-width of the peak. In general, increasing the smoothing ratio improves the signal-to-noise ratio but causes a reduction in amplitude and in increase in the bandwidth of the peak.



The figures above show examples of the effect of three different smooth widths on noisy gaussian-shaped peaks. In the figure on the left, the peak has a (true) height of 2.0 and there are 80 points in the half-width of the peak. The red line is the orignal unsmoothed peak. The three superimposed green lines are the results of smoothing this peak with a triangular smooth of width (from top to bottom) 7, 25, and 51 points. Because the peak width is 80 points, the *smooth ratios* of these three smooths are 7/80 = 0.09, 25/80 = 0.31, and 51/80 = 0.64, respectively. As the smooth width increases, the noise is progressively reduced but the peak height also is reduced slightly. For the largest smooth, the peak width is slightly increased. In the figure on the right, the original peak (in red) has a true height of 1.0 and a half-width of 33 points. (It is also less noisy than the example on the left.) The three superimposed green lines are the results of the same three triangular smooths of width (from top to bottom) 7, 25, and 51 points. But because the peak width in this case is only 33 points, the *smooth ratios* of these three smooths are larger - 0.21, 0.76, and 1.55, respectively. You can see that the peak distortion effect (reduction of peak height and increase in peak width) is greater for the narrower peak because the smooth ratios are higher. Smooth ratios of greater than 1.0 are seldom used because of excessive peak distortion.

Which is the best smooth ratio? It depends on the purpose of the peak measurement. If the objective of the

measurement is to measure the true peak height and width, then smooth ratios below 0.2 should be used. (In the example on the left, the original peak (red line) has a peak height greater than the true value 2.0 because of the noise, whereas the smoothed peak with a smooth ratio of 0.09 has a peak height that is much closer to the correct value). But if the objective of the measurement is to measure the peak position (x-axis value of the peak), much larger smooth ratios can be employed if desired, because smoothing has no effect at all on the peak position (unless the increase in peak width is so much that it causes adjacent peaks to overlap).

In quantitative analysis applications, the peak height reduction caused by smoothing is not so important, because in most cases calibration is based on the signals of standard solutions. If the same signal processing operations are applied to the samples and to the standards, the peak height reduction of the standard signals will be exactly the same as that of the sample signals and the effect will cancel out exactly. In such cases smooth widths from 0.5 to 1.0 can be used if necessary to further improve the signal-to-noise ratio. (The noise is reduced by approximately the square root of the smooth width). In practical analytical chemistry, absolute peak height measurements are seldom required; calibration against standard solutions is the rule. (Remember: the objective of a quantiative spectrophotometric procedure is not to measure absorbance but rather to measure the concentration of the analyte.) It is very important, however, to apply *exactly* the same signal processing steps to the standard signals as to the sample signals, otherwise a large systematic error may result.

SPECTRUM, the freeware signal-processing application that accompanies this tutorial, includes rectangular and triangular smoothing functions for any number of points.

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